

BORON NITROGEN COMPOUNDS

Riley Schaeffer
Indiana University

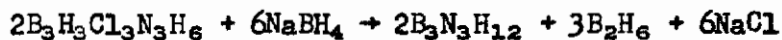
Compounds containing boron and nitrogen have unusual chemical reactivity and provide a challenge in fields for synthesis of new, basically inorganic molecules. The high thermal stability and hydrolytic stability of certain derivatives suggests said further information about the basic nature of boron-nitrogen compounds can be of use in a program concerned with polymeric species.

A relatively high percentage of studies carried out during the last thirty-five years have concentrated on derivatives of the so-called inorganic benzene, $B_3N_3H_6$. In contrast, the majority of studies of boron-phosphorus compounds of a similar character have concentrated on materials bearing a closer resemblance to cycloalkane or alkane structures. Only recently has it become possible to prepare for direct comparison the analogous compounds of the boron-nitrogen series. This paper is concerned with the preparation and properties of the parent molecule itself, hexahydroborazole, $B_3N_3H_{12}$.

Studies thus far carried out serve to focus attention on possible importance of hexahydroborazole in two major lines of investigation. The chemical reactions of hexahydroborazole are frequently more easily controlled than those of borazole itself and can lead to unsymmetrical substitution products. Thermal decomposition or catalytic decomposition affords direct routes to new borazole molecules.

Experimental

A. Preparation of $B_3N_3H_{12}$. - Thirty cc. of dry diethyl ether was condensed into a dry 50 cc. flask at -196° and 2.5 g. (31 mmoles) of pure borazole condensed on top of the ether. The mixture was warmed to -80° and with continuous stirring allowed to absorb an excess (about 120 mmoles) of hydrogen chloride. Within minutes a white precipitate of $B_3N_3H_6 \cdot 3HCl$ was observed. After apparent completion of the reaction the mixture was allowed to slowly warm to room temperature. Ether and excess hydrogen chloride were pumped off and the solid residue was heated to 60° with pumping with a mercury diffusion pump to remove all possible volatile reactants. About 35 cc. of dry diglyme was condensed onto the solid and on warming to room temperature all of the solid dissolved. The flask then was chilled with liquid nitrogen and 4.5g. of sodium borohydride dropped onto the frozen solution under cover of a dry helium stream. The flask then was evacuated again and warmed to room temperature with continuous stirring. Diborane evolution and deposition of a white solid began at once; after several hours a 75% yield of diborane was found to have been produced based on the equation



Volatile ether cleavage products were present as by-products and were discarded without further study. Decantation of the supernatant liquid from the white solid followed by removal of the diglyme by vacuum distillation left a white solid (undoubtedly containing some excess sodium borohydride). On slow warming with continuous pumping a white solid began to sublime between 90 and 100° at pressures below one micron. This substance was resublimed and used for the studies reported below.

B. Analysis. - Samples of the solid substance were treated with 6 M

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aqueous hydrogen chloride for 12 hr. at 100°. Substantially lower acid concentrations or shorter times resulted in incomplete hydrolysis. Hydrogen produced by hydrolysis was measured in the vacuum system, nitrogen was determined by a Kjeldahl procedure and boron was determined by the usual titration in the presence of mannitol following removal of the ammonia. Calcd. for $B_3N_3H_{12}$: B, 37.5%; N, 48.6%; H by hydrolysis, 6.93%. Found: B, 38.4%, 36.9%; N, 47.6%, 47.5%; H, 6.92%, 6.93%.

C. Stability. - When obtained in pure form, hexahydroborazole appears to be remarkably stable towards hydrolysis in comparison with other boron-nitrogen compounds. Thus the compound has been recrystallized from water and yielded only a trace of hydrogen after a solution in 0.5 N hydrochloric acid had been heated for five hours at 115°.

In common with most boron-nitrogen compounds containing hydrogen attached to adjacent atoms, thermal stability of saturated borazole leaves considerable to be desired if the compound itself is considered as a potentially stable molecule. In the present case studies of vapor pressure curves have produced reproducible vapor pressures in the region from 27° to 125° (where the vapor pressure is 5.7 mm.), but hydrogen evolution begins to be important shortly above this temperature. On the other hand, high yields approaching quantitative of borazole have been produced by the thermal decomposition reaction suggesting that substituted hexahydroborazoles can be an important source of new substituted borazoles.

D. Chemical Reactions. - An important type of reaction that has received considerable attention in our laboratory is the reaction of saturated borazole with amides and other potential metallating agents. Study of reaction of sodium amide with saturated borazole in ammonia shows that three moles of hydrogen are rapidly produced per mole of saturated borazole used suggesting complete dehydrogenation to borazole itself. The rate of reaction of borazole with ammonia is too great to permit isolation but in the case of substituted saturated borazoles recovery of the borazole itself has been made. In similar studies reactions of phenyl and butyl lithium with saturated borazole have been carried out in hexane, ether, and tetrahydrofuran to produce solid products which yield borazole when treated with methyl bromide.

Preparation of alkoxy substituted saturated borazoles has been carried out by two separate paths. Saturated borazole is quite soluble in alcohols and relatively stable in the absence of catalysts. In the presence of catalytic quantities of hydrogen chloride, however, a solid product soon precipitates from homogeneous solution in methanol and has been identified as B-monomethoxy saturated borazole. In a parallel reaction, advantage has been taken of the reducing property of the B-H bond to prepare the identical compound by reaction between formaldehyde and saturated borazole and methanol as solvent. In both cases the insolubility of the product in methanol serves to allow preparation in good yields without appreciable further attack of the molecule.

In contrast reaction of saturated borazole with ethanol leads to extensive further substitution without precipitation of a monoethoxy product. The reductive route was successful however. In a typical reaction acetaldehyde and saturated borazole were dissolved in a one to one molar ratio in ethanol and warmed gently with a hair dryer for ten minutes to effect complete solution. On cooling to room temperature a white crystalline material was deposited but no hydrogen had been evolved in the reaction. Recrystallization from ethanol produced a 70% yield of B-monoethoxy saturated borazole. Further studies of the preparations of alkoxy substituted saturated borazoles are in progress.

One of the most remarkable properties thus far observed for saturated borazole is the relatively high stability of the nitrogen-hydrogen bond. In general N-H compounds exchange readily with liquid ammonia, but observations of the nuclear magnetic resonance of saturated borazole in deuterated ammonia show that exchange is effected only over a period of several days at room temperature. Eventually exchange is complete however. Exchange of hydrogen attached to boron can be readily effected by treatment with deuterated diborane.

Nuclear magnetic resonance experiments provide substantial confirmation of the structural assignments above and will be presented.